Proton Magnetic Resonance & Infrared Studies of Interaction of Boron Trihalides & Propionitrile

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Interaction of boron trifluoride, trichloride or tribromide with propionitrile in high vacuum system results in the formation of 1:1 complexes. A significant shift in the signals due to CH$_3$ (triplet) protons in PMR and $\nu$C=N in IR spectra of the complexes, indicate formation of strong donor-acceptor bond. Further, the relative chemical shifts in the PMR spectra suggest that the electron acceptor abilities of BBr$_3$, BCl$_3$ and BF$_3$ follow the order: BBr$_3$ > BCl$_3$ > BF$_3$.

Proton magnetic resonance study$^1$ of exchange reactions between boron trihalide-acetonitrile complexes and excess acetonitrile shows that the strengths of donor-acceptor bond with respect to boron trihalide vary in the order: BBr$_3$ > BCl$_3$ > BF$_3$. The present communication describes the interaction of boron trihalides with propionitrile employing IR and PMR spectroscopy.

Boron trifluoride, trichloride and tribromide and propionitrile were obtained commercially and their interactions carried out in Stocks' high vacuum system$^2$. The reactants were purified prior to the reaction by trap to trap distillation and their purity checked by molecular weights and infrared spectra.

Purified propionitrile (10 mmol) was allowed to distil slowly over pre-condensed purified BX$_3$ (X = F, Cl or Br)(15 mmol) in a trap cooled by liquid nitrogen (-196°C) in the high vacuum system. The liquid nitrogen bath was replaced by that of ice-salt mixture (-4°C) for the reaction of C$_2$H$_5$CN with BCl$_3$ or BBr$_3$ and by that of ethyl bromide-dry ice mixture (-119°C) for the reaction of C$_2$H$_5$CN with BF$_3$. The reaction was allowed to proceed for 1 hr and the excess of unreacted BX$_3$ distilled off. The resulting solid complexes were dried in vacuo at -15°C for 2 hr, yield 90-98%.

The BF$_3$ complex was recrystallised from chloroform (Found: C, 28.6; H, 3.9; N, 11.9; Reqd: C, 29.3; H, 4.1; N, 11.4%). The BCl$_3$ complex was recrystallised from hot chloroform, m.p. 165-67°C (Found: C, 20.2; H, 2.8; N, 8.0; Cl, 62.0; Reqd: C, 20.9; H, 2.9; N, 8.1; Cl, 61.8%). The BBr$_3$ complex was recrystallised from benzene, m.p. 175-80°C (Found: C, 11.0; H, 1.6; N, 4.1; Br, 77.1; Reqd: C, 11.8; H, 1.6; N, 4.6; Br, 78.5%). The PMR spectra of propionitrile and its complexes with boron trihalides were recorded in chloroform or benzene (5% solution) on a Varian NMR spectrometer (model A60D) and their IR spectra in the region 4000-650 cm$^{-1}$ on a Perkin-Elmer (model 521).

The analytical data indicate 1:1 stoichiometry for the complexes and boron atom during adduct formation, changes its hybridisation from $sp^2$ to $sp^3$ resulting in the breaking of the $p_x$-$p_y$ bonds. The relative chemical shifts in the PMR signals in benzene, viz. quartet for CH$_2$ and triplet for CH$_3$-protons get shielded due to their presence in the shielding cone of benzene used as the solvent.

Thus, the CH$_3$ and CH$_2$ signals of CH$_3$CH$_2$CN appeared at 66 Hz (triplet) and 132 Hz (quartet) respectively when the PMR was recorded in chloroform. However, on co-ordination with BF$_3$, BCl$_3$ or BBr$_3$, a regular increase in the downfield shifts of CH$_3$ and CH$_2$ resonances was observed. The CH$_3$ triplet suffered the downfield shifts by 12.5, 19 and 25 Hz and the CH$_2$ quartet by 17.5, 32 and 41 Hz respectively. These results clearly indicate that on coordination of CH$_3$CH$_2$CN with boron trihalides, the charge on C≡N carbon is intensified in the increasing order: C$_2$H$_5$CN-BF$_3$ < C$_2$H$_5$CN-BCl$_3$ < C$_2$H$_5$CN-BBr$_3$.

Conversely in benzene, the CH$_3$ triplet of CH$_3$CH$_2$CN centered at 45.5 Hz shifted upfield by 16.5, 30.5 and 33.5 Hz and the CH$_2$ quartet at 98.5 Hz shifted upfield by 10.5, 30.5 and 35 Hz on coordination with BF$_3$, BCl$_3$ and BBr$_3$ respectively. This increasing order of upfield shifts again manifested a regular enhancement of charge intensity on C≡N carbon in the order: C$_2$H$_5$CN-BF$_3$ < C$_2$H$_5$CN-BCl$_3$ < C$_2$H$_5$CN-BBr$_3$.

The vC≡N in the IR spectrum of C$_2$H$_5$CN appeared at 2247 cm$^{-1}$ or 2244 cm$^{-1}$ in chloroform or benzene. On complexation with boron trihalides, it underwent shift to higher wavenumbers and appeared at $\sim 2340 \pm 5$ cm$^{-1}$ in the spectra of 1:1 complexes. The relative shift of the frequency ($\Delta v$) for BF$_3$; 98, 94 for BCl$_3$; and 98, 96 cm$^{-1}$ for BBr$_3$ complexes in chloroform and benzene respectively does not permit an unambiguous conclusion about the relative acceptor strength of boron trihalides.
The electron acceptor strengths of BCl₃, BBr₃ and BF₃ in exchange reactions between acetonitrile-boron trihalide complexes and excess of acetonitrile also follow the order: BBr₃ > BCl₃ > BF₃ (see ref. 1). The results support the earlier observations of Swanson et al³ and Shriver and Swanson⁴ for corresponding acetonitrile complexes. The order of donor-acceptor bond strengths in propionitrile-boron trihalide complexes as shown above is in agreement with the order suggested by Miller and Onyschuk for trimethylamine-boron trihalide complexes⁵,⁶.

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References